



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

⑪ Publication number:

**0 111 412**

**B1**

J1017 U.S. PTO  
10/053166  
01/15/02

⑫

## EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of patent specification: **30.08.89** ⑯ Int. Cl.<sup>4</sup>: **C 08 C 19/02**  
⑯ Application number: **83307376.0**  
⑯ Date of filing: **05.12.83**

---

④ Polymer hydrogenation process.

---

③ Priority: **08.12.82 CA 417259**

④ Date of publication of application:  
**20.06.84 Bulletin 84/25**

⑤ Publication of the grant of the patent:  
**30.08.89 Bulletin 89/35**

⑥ Designated Contracting States:  
**BE DE FR GB IT NL**

⑦ References cited:  
**GB-A-1 558 491**  
**GB-A-2 070 023**  
**US-A-3 454 644**  
**US-A-3 480 659**  
**US-A-3 898 208**

⑧ Proprietor: **POLYSAR LIMITED**  
**Sarnia Ontario N7T 7M2 (CA)**

⑨ Inventor: **Rempel, Garry Llewellyn**  
**54 Thorndale Drive**  
**Waterloo Ontario (CA)**  
**Inventor: Azizian, Hormoz**  
**225 Harvard Place Apartment 1006**  
**Waterloo Ontario (CA)**

⑩ Representative: **Perry, Robert Edward et al**  
**GILL JENNINGS & EVERY 53-64 Chancery Lane**  
**London WC2A 1HN (GB)**

**EP 0 111 412 B1**

---

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

---

Courier Press, Leamington Spa, England.

## Description

This invention relates to a process for the selective hydrogenation of the carbon-carbon double bonds in a copolymer of a conjugated diene and (meth)acrylonitrile.

5 A variety of processes are known for the hydrogenation of carbon-carbon double bonds in polymers including processes using either homogeneous or heterogeneous catalysts. French Patent 2,421,923 teaches the partial hydrogenation of the double bonds in acrylonitrile - butadiene rubber (NBR) over a palladium/charcoal catalyst. German Offenlegungsschrift 3,046,008 teaches the selective hydrogenation of the double bonds in conjugated diene-containing polymers such as NBR, wherein the catalyst is palladium 10 and at least one other element on a support which may be silica, alumina or activated carbon. German Offenlegungsschrift 3,046,251 teaches a similar process except that the catalyst support is channel or furnace carbon black.

15 GB-A-2070023 discloses a process for the selective hydrogenation of the double bonds in unsaturated organic polymers such as acrylonitrile - butadiene - styrene polymers, when in the form of an aqueous emulsion, using a catalyst such as chlorotris(triphenylphosphine) rhodium in a hydrocarbon solution.

20 U.S. Patent 3,898,208 teaches the hydrogenation of latexes of oil-insoluble polymers of conjugated dienes. The latex is dispersed in a swelling agent for the polymer and hydrogenated in the presence of a catalyst complex which may be a rhodium complex catalyst such as chlorotris(triphenylphosphine) rhodium. The swelling agent must also be a solvent for the catalyst complex.

25 U.S. Patent 3,700,637 teaches that the double bonds in alternating copolymers of conjugated dienes and unsaturated nitriles may be hydrogenated using catalysts such as  $\text{RhCl}(\text{PPh}_3)_3$ ;  $\text{PPh}_3$ =triphenylphosphine.

US-A-3489786 discloses the use of rhodium catalysts in the hydrogenation of residual carbon- 30 carbon unsaturation in copolymers of a conjugated diene.

GB-A-1558491 discloses the hydrogenation of the double bonds in copolymers of a conjugated diene and an  $\alpha,\beta$ -unsaturated carboxylic acid or derivative thereof, for example acrylonitrile, using a homogeneous monovalent or trivalent rhodium halide complex as catalyst, preferably at a temperature of 75 to 115°C and at a pressure of 5 to 10 MPa. The amount of hydrogenation is highly solvent-dependent.

35 US-A-3480659 discloses the selective hydrogenation of double bonds in  $\text{C}_{2-20}$  unsaturated monomers using a homogeneous rhodium hydride complex catalyst, e.g.  $\text{RhH}(\text{PPh}_3)_4$ , with excess ligand ( $\text{PPh}_3$ ), in the presence of hydrogen gas.

IT-A-0912648 discloses that cycloalkadienes and alkadienes may be selectively hydrogenated to the corresponding cycloalkenes and alkenes using a catalyst such as  $\text{RhH}(\text{PPh}_3)_4$ .

40 35 It would be desirable to improve the rate of selective hydrogenation of the carbon-carbon double bonds in copolymers, under relatively mild reaction conditions, while the degree of hydrogenation is relatively insensitive to the type of solvent used.

According to the present invention, in a process for the selective hydrogenation of the carbon-carbon double bonds in a copolymer of a conjugated diene and (meth)acrylonitrile, at a temperature of from 40 to 45 170°C and at a pressure of hydrogen of from 0.05 to 7 MPa, said hydrogenation is carried out in the presence of (i) a catalyst which is a monovalent rhodium hydride complex of the formula  $\text{RhH}(\text{L}_1)_x$  in which  $x$  is 3 or 4 and  $\text{L}_1$  is a ligand compound, (ii) a ligand compound  $\text{L}_2$  and (iii) a solvent for the copolymer, the catalyst and  $\text{L}_2$ , in which the amounts of the catalyst and  $\text{L}_2$  are respectively from 0.05 to 30% by weight and 1 to 25% by weight, based on the weight of the copolymer, in which the  $\text{L}_2$ :catalyst weight ratio is from 0.01:1 to 20:1, and in which  $\text{L}_1$  and  $\text{L}_2$  are the same or different compounds which, when  $x$  is 4, are selected from 5 - phenyl - 5H - dibenzophosphole and compounds of the formula  $\text{PR}_1\text{R}_2\text{R}_3$ , and when  $x$  is 3, are arsenic or antimony compounds of the formula  $\text{AsR}_1\text{R}_2\text{R}_3$  or  $\text{SbR}_1\text{R}_2\text{R}_3$ , wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are independently selected from  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_{6-10}$  aryl and  $\text{C}_{7-12}$  aralkyl.

50 The copolymers containing carbon-carbon double bonds which may be hydrogenated by the process of the present invention are copolymers of a conjugated diene with (meth)acrylonitrile. The copolymers may be of random, alternating or block structure. Suitable conjugated dienes include  $\text{C}_{4-6}$  conjugated dienes such as butadiene, isoprene, dimethylbutadiene and piperylene. Preferred copolymers include butadiene - (meth)acrylonitrile copolymers, isoprene - (meth)acrylonitrile copolymers, and copolymers of butadiene with (meth)acrylonitrile and one or more  $\text{C}_{3-8}$   $\alpha,\beta$ -unsaturated mono- or poly-carboxylic acids such as itaconic, fumaric, maleic, acrylic and methacrylic acids.

55 The solvent used in the process of the present invention may be any organic solvent in which the copolymer, catalyst and second ligand compound  $\text{L}_2$  are soluble and which is not adversely affected by the hydrogenation conditions. Suitable such solvents include the aryl hydrocarbons and their alkyl and halo derivatives such as benzene, toluene, xylene, and chlorobenzene, halogenated aliphatic hydrocarbons such as methylene chloride, 1,1,2 - trichloroethane and dichloroethane, aliphatic ethers such as tetrahydrofuran, certain ketones such as acetone, and mixtures thereof. Acetone is reduced to some extent to form isopropanol under the reaction conditions but this does not interfere with the desired hydrogenation of the copolymer. Other ketones may be reduced to a greater extent with the possibility of precipitating the copolymer from solution and thereby limiting the amount of hydrogenated copolymer produced. Such ketones should therefore be used with caution.

A first preferred embodiment of the process of the present invention is a homogeneous solution hydrogenation process wherein the hydrogenation is carried out with the copolymer, catalyst and second ligand compound  $L_2$  dissolved in the solvent. The copolymer may first be dissolved in the solvent and the resulting solution degassed. The catalyst and the second ligand compound may then be added to and dissolved in the solution contained in a reaction vessel and the reaction vessel pressurized with hydrogen gas. Alternatively, the copolymer solution contained in a reaction vessel may be pressurized with hydrogen followed by the addition of catalyst and second ligand compound to the reaction vessel. Then the reaction vessel is heated rapidly to the desired temperature, agitation is initiated and the hydrogenation reaction allowed to proceed for the desired length of time, the pressure of hydrogen preferably but not necessarily being held constant. Upon completion of the reaction, the hydrogenated copolymer may be recovered by any convenient method well known in the art. For example, the reaction mixture may be mixed with an alcohol or contacted with hot water and/or steam in order to precipitate the copolymer which is then separated, washed if desired, and dried e.g. under vacuum in a hot air oven. If desired, the catalyst may be recovered by the method described in U.S. Patent 3,545,963.

15 The concentration of copolymer in the solution is from 1 to 20 per cent by weight and preferably from 1 to 10 per cent by weight, based on the total weight of the solution.

Catalyst is used in an amount from 0.05 to 20 per cent by weight based on the weight of the copolymer and preferably from 0.1 to 15 per cent by weight. Suitable catalysts include hydridotetrakis(trimethyl-, triethyl- and triphenylphosphine) rhodium, and hydridotris(triphenylarsine) rhodium.

20 A second ligand compound  $L_2$  is added to the reaction mixture. It is generally considered that the added ligand compound acts to stabilize the catalyst. While the second ligand compound  $L_2$  may be different from the first ligand compound  $L_1$  present in the catalyst, it is preferred that  $L_1$  and  $L_2$  are the same. Suitable ligand compounds include trimethyl-, triethyl- and triphenylphosphine and triphenylarsine. It is preferred that both  $L_1$  and  $L_2$  are triphenylphosphine and that the catalyst therefore is hydridotetrakis(tri-25 phenylphosphine) rhodium. The amount of the second ligand compound which is added is from 1 to 25 per cent by weight based on the weight of the copolymer and preferably from 3 to 20 per cent by weight. The weight ratio of second ligand compound to catalyst is from 0.6:1 to 20:1, and preferably from 0.6:1 to 10:1.

The reaction vessel is pressurized with gaseous hydrogen to a pressure of hydrogen of from 0.05 to 7 MPa and preferably from 0.05 to 3 MPa. It is preferred that pure hydrogen gas be used. However, 30 hydrogen gas containing very small amounts of inert gases such as nitrogen may also be used.

35 The hydrogenation reaction is carried out at a temperature of from 40° to 170°C and preferably from 80° to 160°C. Under these conditions, essentially complete hydrogenation of the carbon-carbon double bonds may be achieved in from 1 to 50 hours. Preferred reaction times may be from 2 to 10 hours. By using suitable conditions of time and temperature it is possible to obtain copolymers which are only partially hydrogenated. The amount of hydrogenation may be adjusted to suit the requirements for the product required.

40 In a second preferred embodiment of the process of the present invention, the copolymer is hydrogenated in the form of an aqueous emulsion. Copolymers of conjugated dienes and copolymerizable monomers are frequently manufactured by a free radical emulsion process. The copolymer emulsion so formed may be hydrogenated using the process of the present invention. Copolymers made by other methods may be emulsified by any of the processes well known to the art.

45 The copolymer emulsion is placed in a reaction vessel and diluted with water if necessary to provide an emulsion containing from 3 to 40 and preferably from 5 to 10 per cent by dry weight of copolymer based on the total weight of the emulsion. Sufficient solvent is added to the reaction vessel so that the dry weight of copolymer is from 1 to 20 and preferably from 3 to 10 per cent based on the total weight of the solvent and copolymer. In this embodiment, mixtures of solvents are preferred, such as toluene or chlorobenzene with acetone, especially 1:1 mixtures by volume.

50 The contents of the reaction vessel are degassed and the reaction vessel is purged and then the catalyst and the second ligand compound are added. The reaction vessel is pressurized with hydrogen, heated rapidly to reaction temperature, and stirring commenced. The product is recovered following completion of the hydrogenation as described above. The preferred hydrogen pressure is from 1.4 to 4 MPa and the preferred reaction temperature is from 80° to 120°C. In this embodiment, the preferred amount of catalyst is from 1 to 2 per cent by weight based on the copolymer and the preferred catalyst is hydridotetrakis(triphenylphosphine) rhodium. The preferred amount of the second ligand compound is from 10 to 20 per cent by weight based on the copolymer and the preferred ligand compound is triphenylphosphine. The preferred weight ratio of the ligand compound to the catalyst is from 5:1 to 15:1. Suitable reaction times may be from 10 to 40 hours. Under the preferred conditions of temperature and pressure, essentially complete hydrogenation of the carbon-carbon double bonds may be achieved in from 12 to 25 hours. Partially hydrogenated copolymers may be obtained by using suitable conditions of time and temperature.

55 The hydrogenated products of the process of the present invention are vulcanizable elastomers the vulcanizates of which may be used in applications requiring resistance to oxidizing conditions at elevated temperatures for extended periods of time as for example in the various hoses and seals in the engine compartment of an automobile. These hydrogenated copolymers may be vulcanized using conventional peroxide or peroxide/sulfur curing systems. It is preferred to use vulcanizates in which from 50 to 99.95 per

EP 0 111 412 B1

cent, more preferably from 95 to 99.95 per cent, and most preferably from 99 to 99.95 per cent of the carbon-carbon double bonds in the copolymer have been hydrogenated.

The following examples illustrate the present invention and are not intended to be limiting.

5 Example 1

In this and succeeding examples, the copolymers which were hydrogenated are listed in Table 1. The composition figures are given in per cent by weight.

TABLE 1

	Copolymer	Composition
10	I	An acrylonitrile-butadiene copolymer containing 66 per cent by weight butadiene sold under the trade name Krync 34.50 by Polysar Limited.
15	II	An acrylonitrile-butadiene copolymer containing 60 per cent by weight butadiene sold under the trade name Krync 40.65 by Polysar Limited.
20	III	An acrylonitrile-isoprene copolymer containing 66 per cent by weight isoprene sold under the trade name Krync 833 by Polysar Limited.
25	IV	A carboxylated acrylonitrile-butadiene copolymer containing 64 per cent by weight butadiene sold under the trade name Krync 221 by Polysar Limited.
30	V	A carboxylated acrylonitrile-butadiene copolymer containing 66 per cent by weight butadiene sold under the trade name Krync 110C by Polysar Limited.

35 This example illustrates a homogeneous solution hydrogenation process of the present invention. Each of the six copolymers listed in Table 1 was hydrogenated separately using hydridotetrakis(triphenylphosphine) rhodium as catalyst, triphenylphosphine as ligand compound and chlorobenzene as solvent.

The copolymer was dissolved in the solvent under an inert atmosphere of nitrogen or argon and the solution so formed was then transferred to a 1.5 l glass lined autoclave, the autoclave assembled and the 40 solution degassed by bubbling the inert gas through the solution for 10 minutes. The autoclave was purged repeatedly by pressuring with inert gas for periods of 5 minutes and then releasing the pressure. The autoclave was opened briefly, the catalyst and ligand compound added, and the autoclave closed and pressured with hydrogen to 2.8 MPa for a period of 5 minutes. The pressure was released and then the autoclave was repressured with hydrogen to the desired reaction pressure and heated rapidly over a period 45 of 15-20 minutes to the reaction temperature. Stirring was initiated and the reaction allowed to proceed for the desired length of time. Hydrogen gas was added as required to maintain the pressure essentially constant throughout the reaction period.

50 After the desired reaction period, the autoclave was cooled rapidly in an ice-salt bath, depressured and opened. A volume of isopropanol equal to about 2-4 times the volume of the solvent used in the reaction was added to the reaction product. The hydrogenated product which precipitated out of solution was separated by filtration, washed with isopropanol and dried under vacuum at 50°C.

The product was analyzed by proton NMR to determine the amount of hydrogenation of the 55 carbon-carbon double bonds. Analysis by carbon-13 NMR showed that no hydrogenation occurred of the nitrile groups of Copolymers I through V of Table 1. Analysis by IR spectroscopy showed that no hydrogenation occurred of the acid groups of Copolymers IV and V.

The amounts of catalyst, second ligand compound, solvent and copolymer used are shown in Table 2. In this example and in those that follow, the concentration of copolymer in the solution is in per cent by weight based on the total weight of the solution while the concentration of the catalyst and ligand compound are in per cent by weight based on the copolymer. The per cent hydrogenation figures given are the per cent of the carbon-carbon double bonds of the copolymer which have been hydrogenated. When a value of 99+ is given, the amount of hydrogenation is greater than 99 per cent and less than or equal to 99.95 per cent, i.e. essentially complete hydrogenation.

TABLE 2

Run No.	Copolymer		Concentration		Hydrogen pressure (MPa)	Reaction temp. (°C)	Solvent volume (ml)	Reaction time (hr)	Per cent hydrogenation
	Type	conc.	Catalyst	Ligand					
1	I	6.0	1.0	10	2.8	110	700	4.0	99+
2	I	2.5	1.0	10	1.4	110	350	4.5	99+
3	I	2.5	1.0	10	2.8	97	350	4.0	97
4	I	2.5	1.0	10	2.8	160	350	1.0	99+
5	I	2.5	0.5	5	2.8	110	350	2.0	99+
6	II	6.0	1.0	10	2.8	87	700	4.0	91
7	II	6.0	1.0	10	2.8	90	700	3.6	85
8	II	6.0	1.0	10	2.8	110	700	3.5	99+
9	III	2.5	1.0	10	2.8	110	350	4.5	51
10	III	2.5	1.0	10	2.8	130	350	15.0	90
11	IV	6.0	0.5	5	2.8	110	700	7.0	94
12	IV	2.5	1.0	10	2.8	110	350	6.5	99+
13	V	6.0	0.5	5	2.8	110	700	3.0	99+
14	VI	6.0	0.5	5	2.8	110	700	3.0	99+

EP 0 111 412 B1

Example 2

This example illustrates the hydrogenation of a copolymer in the form of an aqueous emulsion and in the presence of a hydrocarbon solvent mixture. To a 1.5 l glass lined autoclave were added in a first run 50 ml of an aqueous latex of Copolymer I from Table 1 which contained about 10 g of copolymer, 75 ml of water and 75 ml of toluene. Stirring was initiated and 75 ml of acetone were then slowly added and the system was degassed and purged as described in Example 1. 0.2 g of hydridotetrakis(triphenylphosphine) rhodium and 2.0 g of triphenylphosphine were added to the autoclave followed by pressuring with hydrogen gas to 2.8 MPa. The autoclave was heated rapidly to 110°C. Samples were withdrawn after 5 and 7 hours reaction time. Proton NMR indicated that 58 per cent (5 hours) and 71 per cent (7 hours) of the carbon-carbon double bonds in the copolymer had been hydrogenated.

In a second run, the same procedure was followed except that 250 ml of toluene, 125 ml of acetone, 0.1 g of hydridotetrakis(triphenylphosphine) rhodium and 1.0 g of triphenylphosphine were used. A sample was withdrawn after 8 hours and analyzed by proton NMR which showed that 51 per cent of the carbon-carbon double bonds had been hydrogenated.

In a third run the same procedure was used except that 150 ml of water were added along with 150 ml of chlorobenzene in place of the toluene followed by 150 ml of acetone. A sample was withdrawn after 16 hours and analyzed by proton NMR which showed that 98 per cent of the carbon-carbon double bonds had been hydrogenated.

In a fourth run the procedure of the third run was followed using twice as much of each component in the hydrogenation reaction. A sample was withdrawn after 20 hours and proton NMR analysis showed that 99+ per cent of the carbon-carbon double bonds had been hydrogenated.

Example 3

This example illustrates the use of a homogeneous solution hydrogenation process of the present invention to produce hydrogenated copolymers with varying degrees of hydrogenation of the carbon-carbon double bonds. Two runs were made in which the reaction temperature was increased slowly to a maximum and then maintained at this temperature. Samples were withdrawn while the temperature was increasing and after the maximum was reached and were analyzed by proton NMR for the per cent of carbon-carbon double bonds which had been hydrogenated.

In a first run, 10.0 g of Copolymer I of Table 1 were dissolved in 350 ml of chlorobenzene and the solution added to the autoclave as in Example 1 followed by degassing and purging with nitrogen, 0.1 g of the catalyst hydridotetrakis(triphenylphosphine) rhodium and 1.0 g of triphenylphosphine were added and the autoclave pressured to 2.8 MPa with hydrogen. The autoclave was heated from room temperature to 97°C over a period of 3.5 hr and maintained at 97°C for a further 0.7 hr after which the reaction was terminated and the product recovered as described in Example 1. Analytical results are shown in Table 3.

TABLE 3

40	Reaction time (hr)	Reaction temperature (°C)		Per cent hydrogenation
		1.5	60	
45	2.0	70	41	
	2.5	83	55	
	3.0	90	79	
	3.3	92	85	
50	3.5	97	94	
	4.2	97	99+	

In a second run, 700 ml of a 6.0 per cent by weight solution in chlorobenzene of Copolymer II from Table 1 were hydrogenated as in the first run in the presence of 0.50 g of the same catalyst and 5.0 g of triphenylphosphine. The autoclave was pressured to 2.8 MPa of hydrogen and heated to 87°C over a period of 3.0 hr and then maintained at this temperature for an additional 1.2 hr. Analytical results are given in Table 4.

## EP 0 111 412 B1

TABLE 4

	Reaction time	Reaction temperature (°C)	Per cent hydrogenation
5	1.5	67	22
	2.0	76	36
10	2.3	80	41
	3.0	87	60
	3.3	87	76
15	4.2	87	91

These runs both demonstrate that by stopping the reaction at any desired point and recovering the product, one may obtain a partially hydrogenated product.

## 20 Example 4

This example illustrates a homogeneous solution hydrogenation process of the present invention using a range of solvents. The procedure used was that described in Example 1 except that only Copolymer I from Table 1 was hydrogenated in each of the runs. In each run, the hydrogen pressure was 2.8 MPa and the reaction temperature was 110°C. Data are given in Table 5.

TABLE 5

Run No.	Copolymer conc.	Concentration		Solvent				Per cent hydrogenation
		Catalyst	Ligand	Type	Volume (ml)	Reaction time (hr)		
1	2.5	0.5	5	chlorobenzene	350	2.0		99+
2	2.5	1.0	10	p-xylene	450	2.5		75
3	2.5	0.7	7	acetone	500	4.0		99+
4	2.5	1.0	10	benzene	350	8.5		98
5	2.3	2.0	20	toluene	500	8.0		93
6	2.5	2.0	20	1,1,2-trichloroethane	272	7.0		99+

## Example 5

This example illustrates a homogeneous solution hydrogenation process of the present invention using a range of catalyst and second ligand compound concentrations and a range of hydrogen pressures. The procedure used was that of Example 1 except that only Copolymers I and IV from Table 1 were hydrogenated. In each run the reaction temperature was 110°C and the solvent was chlorobenzene. Data are given in Table 6.

55

60

65

TABLE 6

Run No.	Copolymer		Concentration		Hydrogen pressure (MPa)	Solvent volume (ml)	Reaction time (hr)	Per cent hydrogenation
	Type	Conc.	Catalyst	Ligand				
1	I	2.5	1.0	10	1.4	350	4.5	99+
2	I	2.5	1.0	5	2.8	350	2.5	99+
3	I	2.5	0.5	5	2.8	350	2.0	99+
4	I	2.5	0.1	1	2.8	350	6.0	88
5	I	2.5	1.0	10	0.5	350	3.0	99+
6	IV	6.0	0.5	5	2.8	700	7.0	94
7	IV	2.5	1.0	10	2.8	350	6.5	99+
8	IV	5.7	1.5	15	2.8	800	6.0	99+

## Example 6

Copolymer 1 of Table 1 was hydrogenated in separate runs using two different catalyst-ligand compound combinations. In a first run, the catalyst was hydridotetrakis(triphenylphosphine) rhodium and the ligand compound was triphenylphosphine. In a second run, the catalyst was hydridotris(triphenylarsine) rhodium and the ligand compound was triphenylarsine.

Both runs were carried out using a constant pressure gas uptake apparatus which was very similar to that described by J. L. Bolland in "The Proceedings of the Royal Society", Volume A186, p. 218-236, 1946. The procedure used was that 0.18 g of Copolymer 1 from Table 1 was dissolved under a nitrogen atmosphere in 10 ml of chlorobenzene contained in a 50 ml two-necked glass flask. The side arm of the flask was equipped with a quick fit extended cone with an attached hook from which could be suspended a glass bucket. The amounts of catalyst and second ligand compound shown in Table 7 were placed in the bucket which was then suspended from the hook. The cone with suspended bucket was inserted into the side arm of the flask. The solution in the flask was degassed under vacuum by repeated freezing with liquid nitrogen and thawing. Hydrogen gas was then admitted to the flask to provide a pressure of about 0.06 MPa. The flask was immersed in a silicone oil bath, maintained at  $80^\circ \pm 0.1^\circ \text{C}$  and a piston rod driven by a variable speed electric motor was attached to the flask to that operation of the motor could provide a rapid shaking motion to the flask and its contents. The hydrogen pressure was adjusted to the reaction pressure shown in Table 7, operation of the motor initiated and the flask and its contents shaken for about 0.5 hour to ensure equilibrium of the hydrogen dissolved in the copolymer solution and that in the gaseous phase. The cone was turned so that the bucket and its contents fell into the solution. Shaking was resumed and as the reaction proceeded, hydrogen gas was introduced into the system to maintain the initial pressure. The hydrogen consumption was monitored by the rise in the mercury level in the precision bore tubing of the apparatus. After the reaction time shown in Table 7, the reaction mixture was cooled to room temperature and the flask disconnected from the apparatus. 20 ml of isopropanol were added to the reaction mixture, and the hydrogenated copolymer product which precipitated out was separated by proton filtration, washed with isopropanol and dried under vacuum at  $50^\circ \text{C}$ . This material was analyzed by proton NMR to determine the amount of hydrogenation of the carbon-carbon double bonds. Analysis by carbon 13 NMR showed that no hydrogenation of the nitrile groups in the copolymer had occurred.

TABLE 7

Run	Concentration		Hydrogen pressure (MPa)	Reaction time (hours)	Percent hydrogenation
	Catalyst	Ligand			
1	14	9.5	0.068	3.8	99+
2	13	11	0.068	24	50

## Example 7

This example illustrates that a hydrogenated copolymer of butadiene and acrylonitrile may be cured using a peroxide/sulfur vulcanization system to produce vulcanizates having useful elastomeric properties even after air aging for up to 1,000 hours at  $150^\circ \text{C}$ . A 10 g sample of a hydrogenated copolymer, prepared by hydrogenating copolymer 1 of Table 1 to produce a copolymer in which 99.1 per cent of the carbon-carbon double bonds were hydrogenated, was placed on a two-roll micro mill and compounded in the conventional manner by the addition of the compounding ingredients shown in Table 8. The sample was oven cured at  $180^\circ \text{C}$  for 5.5 minutes to produce the optimum state of cure as measured using a Monsanto Oscillating Disc Rheometer. The tensile properties shown in Table 9 were then measured according to ASTM-D412-80. Hardness properties were measured using a Type A Shore durometer according to ASTM-D2240-81. Hot air aging was carried out according to ASTM-D865-81 at  $150^\circ \text{C}$ .

55

60

65

TABLE 8

	Compounding ingredient	Amount (parts by weight per 100 parts by weight of copolymer)
5	p-Cumyldiphenyl amine	2.0
10	2-Mercaptobenzimidazole	2.0
15	Sulfur	0.1
20	Zinc oxide	5.0
25	Precipitated amorphous anhydrous silica	50
30	Ether thioether plasticizer	10
35	Processing aid (sold under trade name TE 80 by Technical Processing Inc.)	1.0
40	N,N'-m-phenylenedimaleimide	1.0
45	2,5-Dimethyl-2,5-di-t-butylperoxyhexane	3.5

TABLE 9

	Air aged for (hours)					
	Physical property	0	74	168	504	1,000
30	Hardness	70	72	78	80	*
35	Tensile stress (MPa)					
35	—at 100% elongation	1.0	2.5	3.4	5.4	8.6
40	—at 300% elongation	2.9	5.9	8.3	13.2	14.7
40	—at rupture	14.2	23.0	21.6	20.1	16.4
45	Elongation, % at rupture	860	750	700	600	380

\*not measured

## Claims

1. A process for the selective hydrogenation of the carbon-carbon double bonds in a copolymer of a conjugated diene and (meth)acrylonitrile, at a temperature of from 40 to 170°C and at a pressure of hydrogen of from 0.05 to 7 MPa, characterised in that said hydrogenation is carried out in the presence of (i) a catalyst which is a monovalent rhodium hydride complex of the formula  $\text{RhH}(\text{L}_1)_x$  in which x is 3 or 4 and  $\text{L}_1$  is a ligand compound, (ii) a ligand compound  $\text{L}_2$  and (iii) a solvent for the copolymer, the catalyst and  $\text{L}_2$ , in which the amounts of the catalyst and  $\text{L}_2$  are respectively from 0.05 to 30% by weight and 1 to 25% by weight, based on the weight of the copolymer, in which the  $\text{L}_2$ :catalyst weight ratio is from 0.01:1 to 20:1, and in which  $\text{L}_1$  and  $\text{L}_2$  are the same or different compounds which, when x is 4, are selected from 5-phenyl-5H-dibenzophosphole and compounds of the formula  $\text{PR}_1\text{R}_2\text{R}_3$ , and when x is 3, are arsenic or antimony compounds of the formula  $\text{AsR}_1\text{R}_2\text{R}_3$  or  $\text{SbR}_1\text{R}_2\text{R}_3$ , wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are independently selected from  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_{6-10}$  aryl and  $\text{C}_{7-12}$  aralkyl.
2. A process according to claim 1, conducted as a homogeneous solution hydrogenation process, in which the catalyst and  $\text{L}_2$  are dissolved in the solvent.
3. A process according to claim 2, in which the solvent is selected from chlorobenzene, toluene, xylene, acetone, 1,1,2-trichloroethane and mixtures thereof, and in which the solution contains from 1 to 20% w/w of the copolymer.
4. A process according to claim 2 or claim 3, in which the weights of the catalyst and  $\text{L}_2$  are respectively

from 0.3 to 15 and 3 to 20% by weight of the copolymer, and the  $L_2$ :catalyst weight ratio is from 0.6:1 to 10:1.

5. A process according to any of claims 2 to 4, in which the temperature is from 80 to 160°C and the pressure of hydrogen is from 0.05 to 3 MPa.

5. A process according to claim 1, conducted in an aqueous emulsion containing from 3 to 40% w/w of the copolymer (dry weight).

7. A process according to claim 6, in which the solvent is a mixture of toluene or chlorobenzene with acetone, and in which the emulsion contains from 1 to 20% by weight of the copolymer (dry weight), based on the total weight of the copolymer and the solvent.

10. A process according to claim 6 or claim 7, in which the weights of the catalyst and  $L_2$  are respectively from 1 to 2 and 10 to 20% by weight of the copolymer, and the  $L_2$ :catalyst weight ratio is from 5:1 to 15:1.

9. A process according to any of claims 6 to 8, in which the temperature is from 80 to 120°C and the pressure of hydrogen is from 1.4 to 4 MPa.

10. A process according to any preceding claim, in which  $L_1$  and  $L_2$  are the same and are selected from trimethylphosphine, triethylphosphine, triphenylphosphine and triphenylarsine.

15. 11. A process according to claim 10, in which  $L_1$  and  $L_2$  are triphenylphosphine.

12. A process according to any preceding claim, in which the copolymer is of butadiene with (meth)acrylonitrile and, optionally, one or more of itaconic acid, fumaric acid, acrylic acid, methacrylic acid and maleic acid; or isoprene with acrylonitrile or methacrylonitrile.

20. 13. A process according to claim 12, in which the copolymer is a butadiene-acrylonitrile copolymer.

#### Patentansprüche

25. 1. Verfahren zur selektiven Hydrierung der Kohlenstoff - Kohlenstoff - Doppelbindungen in einem Copolymer aus einem konjugierten Dien und (Meth)Acrylnitril bei einer Temperatur von 40°C bis 170°C und bei einem Wasserstoff-Druck von 0,05 bis 7 MPa, dadurch gekennzeichnet, daß die Hydrierung durchgeführt wird in Gegenwart

(i) eines Katalysators, der ein Hydrid-Komplex des einwertigen Rhodiums der Formel  $(RhH(L_1))_x$  ist, in der  $x \geq 3$  oder 4 ist und  $L_1$  eine Liganden-Verbindung ist,

(ii) einer Liganden-Verbindung  $L_2$  und

(iii) einem Lösungsmittel für das Copolymer, den Katalysator und  $L_2$ ,

worin die Mengen des Katalysators und von  $L_2$  und 0,05 bis 30 Gew.-% bzw. 1 bis 25 Gew.-%, bezogen auf das Gewicht des Copolymer, betragen, worin das Gewichtsverhältnis  $L_2$ :Katalysator 0,01:1 bis 20:1 beträgt und worin  $L_1$  und  $L_2$  die gleichen oder verschiedene Verbindungen sind, die, wenn  $x = 4$  ist, aus 5 - Phenyl - 5H - dibenzophosphol und Verbindungen der Formel  $PR_1R_2R_3$  ausgewählt sind und, wenn  $x = 3$  ist, Arsen- oder Antimon-Verbindungen der Formeln  $AsR_1R_2R_3$  oder  $SbR_1R_2R_3$  sind, worin  $R_1$ ,  $R_2$  und  $R_3$  unabhängig voneinander aus  $CH_3$ ,  $C_2H_5$ ,  $C_{6-10}$ -Aryl und  $C_{7-12}$ -Araalkyl ausgewählt sind.

2. Verfahren nach Anspruch 1, durchgeführt als Verfahren der Hydrierung in homogener Lösung, wobei der Katalysator und  $L_2$  in dem Lösungsmittel gelöst werden.

3. Verfahren nach Anspruch 2, worin das Lösungsmittel aus Chlorbenzol, Benzol, Toluol, Xylol, Aceton, 1,1,2 - Trichloroethan und deren Mischungen ausgewählt wird und worin die Lösung 1 bis 20 Gew./Gew.-% des Copolymer enthält.

4. Verfahren nach Anspruch 2 oder Anspruch 3, worin die Gewichte des Katalysators und  $L_2$  0,2 bis 15 bzw. 3 bis 20 Gew.-%, bezogen auf das Copolymer, betragen und das Gewichtsverhältnis  $L_2$ :Katalysator 0,6:1 bis 10:1 beträgt.

5. Verfahren nach irgendeinem der Ansprüche 2 bis 4, worin die Temperatur 80°C bis 160°C beträgt und der Wasserstoff-Druck 0,05 bis 3 MPa beträgt.

6. Verfahren nach Anspruch 1, durchgeführt in einer wässrigen, 3 bis 40 Gew./Gew.-% des Copolymer (Trockengewicht) enthaltenden Emulsion.

7. Verfahren nach Anspruch 6, worin das Lösungsmittel eine Mischung aus Toluol oder Chlorbenzol mit Aceton ist und worin die Emulsion 1 bis 20 Gew./Gew.-% des Copolymer (Trockengewicht), bezogen auf das Gesamtgewicht des Copolymer und des Lösungsmittels, enthält.

8. Verfahren nach Anspruch 6 oder Anspruch 7, worin die Gewichte des Katalysators und  $L_2$  1 bis 2 bzw. 10 bis 20 Gew.-%, bezogen auf das Copolymer, betragen und das Gewichtsverhältnis  $L_2$ :Katalysator 5:1 bis 15:1 beträgt.

9. Verfahren nach irgendeinem der Ansprüche 6 bis 8, worin die Temperatur 80°C bis 120°C beträgt und der Wasserstoff-Druck 1,4 bis 4 MPa beträgt.

10. Verfahren nach irgendeinem der vorhergehenden Ansprüche, worin  $L_1$  und  $L_2$  gleich sind und aus Trimethylphosphin, Triethylphosphin, Triphenylphosphin und Triphenylarsin ausgewählt sind.

11. Verfahren nach Anspruch 10, worin  $L_1$  und  $L_2$  Triphenylphosphin sind.

12. Verfahren nach irgendeinem der vorhergehenden Ansprüche, worin das Copolymer eines aus Butadien mit (Meth)Acrylnitril und ggf. einer oder mehreren der Verbindungen Itaconsäure, Fumarsäure, Acrylsäure, Methacrylsäure und Maleinsäure oder aus Isopren mit Acrylnitril oder Methacrylnitril ist.

13. Verfahren nach Anspruch 12, worin das Copolymer ein Butadien-Acrylnitril-Copolymer ist.

Revendications

1. Procédé d'hydrogénéation sélective des doubles liaisons carbone-à-carbone d'un copolymère d'un diène conjugué et de (méth)acrylonitrile à une température de 40 à 170°C et à une pression d'hydrogène de 0,05 à 7 MPa, caractérisé en ce que ladite hydrogénéation est conduite en présence (i) d'un catalyseur qui est un complexe d'hydrure de rhodium monovalent de formule  $\text{RhH}(\text{L}_1)_x$  dans laquelle  $x$  a la valeur 3 ou 4 et  $\text{L}_1$  est un composé ligand, (ii) d'un composé ligand  $\text{L}_2$  et (iii) d'un solvant pour le copolymère, le catalyseur et  $\text{L}_2$ , dans lequel les quantités de catalyseur et de  $\text{L}_2$  sont, respectivement, de 0,05 à 30% en poids et de 1 à 25% en poids, sur la base du poids du copolymère, dans lequel le rapport pondéral  $\text{L}_2$ :catalyseur va de 0,01:1 à 20:1 et dans lequel  $\text{L}_1$  et  $\text{L}_2$  sont des composés identiques ou différents qui, lorsque  $x$  est égal à 4, sont choisis entre le 5 - phényl - 5H - dibenzophosphole et des composés de formule  $\text{PR}_1\text{R}_2\text{R}_3$ , et lorsque  $x$  est égal à 3, il s'agit de composés d'arsenic ou d'antimoine de formule  $\text{AsR}_1\text{R}_2\text{R}_3$  ou  $\text{SbR}_1\text{R}_2\text{R}_3$  dans laquelle  $\text{R}_1$ ,  $\text{R}_2$  et  $\text{R}_3$  sont choisis, indépendamment, entre des radicaux  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , aryle en  $\text{C}_6$  à  $\text{C}_{10}$  et aralkyle en  $\text{C}_7$  à  $\text{C}_{12}$ .
2. Procédé suivant la revendication 1, mis en oeuvre comme un procédé d'hydrogénéation en solution homogène dans lequel le catalyseur et  $\text{L}_2$  sont dissous dans le solvant.
3. Procédé suivant la revendication 2, dans lequel le solvant est choisi entre le chlorobenzène, le benzène, le toluène, le xylène, l'acétone, le 1,1,2 - trichloréthane et leurs mélanges et dans lequel la solution contient 1 à 20% en poids/poids du copolymère.
4. Procédé suivant la revendication 2 ou la revendication 3, dans lequel les poids respectifs du catalyseur et de  $\text{L}_2$  sont de 0,3 à 15 et de 3 à 20% en poids du copolymère et le rapport pondéral  $\text{L}_2$ :catalyseur va de 0,6:1 à 10:1.
5. Procédé suivant l'une quelconque des revendications 2 à 4, dans lequel la température va de 80 à 160°C et la pression d'hydrogène va de 0,05 à 3 MPa.
6. Procédé suivant la revendication 1, mis en oeuvre dans une émulsion aqueuse contenant 3 à 40% en poids/poids du copolymère (poids sec).
7. Procédé suivant la revendication 6, dans lequel le solvant est un mélange de toluène ou de chlorobenzène avec de l'acétone et dans lequel l'émulsion contient 1 à 20% en poids du copolymère (poids sec), sur la base du poids total du copolymère et du solvant.
8. Procédé suivant la revendication 6 ou la revendication 7, dans lequel les poids respectifs du catalyseur et de  $\text{L}_2$  sont de 1 à 2 et 10 à 20% par rapport au poids du copolymère et le rapport pondéral  $\text{L}_2$ :catalyseur va de 5:1 à 15:1.
9. Procédé suivant l'une quelconque des revendications 6 à 8, dans lequel la température va de 80 à 120°C et la pression d'hydrogène est de 1,4 à 4 MPa.
10. Procédé suivant l'une quelconque des revendications précédentes, dans lequel  $\text{L}_1$  et  $\text{L}_2$  sont identiques et sont choisis entre la triméthylphosphine, la triéthylphosphine, la triphénylphosphine et la triphénylarsine.
11. Procédé suivant la revendication 10, dans lequel  $\text{L}_1$  et  $\text{L}_2$  sont la triphénylphosphine.
12. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le copolymère est un copolymère de butadiène avec le (méth)acrylonitrile et, à titre facultatif, un ou plusieurs des monomères acide itaconique, acide fumrique, acide acrylique, acide méthacrylique et acide maléique; ou un copolymère d'isoprène avec l'acrylonitrile ou le méthacrylonitrile.
13. Procédé suivant la revendication 12, dans lequel le copolymère est un copolymère butadièneacrylonitrile.

45

50

55

60

65